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Crystal structure of the ethanol adduct of *N*-triphenylstannyl-1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide

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Abstract

N-Triphenylstannyl-1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide crystallizes from ethanol as the adduct, $[\overline{SO_2C_6H_4C(O)N}Sn(C_6H_5)_3 \cdot C_2H_5OH]$, in the monoclinic space group $P2_1$ with a 9.460(2), b 16.338(1), c 9.580(2) Å, β 113.76(2)°; $Z = 2$. The molecule is monomeric and five-coordinate at tin. The coordination geometry is distorted *trans*-C_3SnNO trigonal bipyramidal, with the *ipso*-carbons (Sn–C 2.111(5), 2.120(8), 2.128(7) Å) of the phenyl rings lying in the equatorial plane and the axial positions occupied by the imido nitrogen atom of the saccharin (Sn–N 2.240(7) Å) and the ethanolic oxygen atom (Sn–O 2.394(8) Å). The tin atom is displaced from the equatorial plane by 0.221(1) Å in the direction of the apical nitrogen. The compound is an unusual example of an organotin complex containing coordinated ethanol.

Introduction

The artificial sugar substitute, 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide (saccharin) [1], forms a series of alkali [2,3], alkaline earth [2], transition metal [4–9] and main group metal [10–12] salts. To date, only one organometallic saccharin compound appears to have been crystallographically studied, namely trimethyltin saccharin hydrate [13], which is five-coordinate at the tin atom, with the trimethylstannyl unit bonded to the saccharin nitrogen as well as to the water molecule. The synthesis of anhydrous trimethyltin saccharin has been claimed [13–15], but although the compound is probably also five-coordinate, the question of whether coordination is via carbonyl versus sulfonyl oxygen in this and other triorganotin saccharins has not been unambiguously resolved by spectroscopic studies [15].

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Neither carbonyl nor sulfonyl ligands are strong Lewis bases towards organotin acceptors. Carbonyl donors are basic if the ligand is capable of charge dispersal [16]; sulfonyl groups lack this capability, and sulfonyl oxygen–tin bonds are generally weak [17,18]. However, since the saccharin ligand is known to coordinate through either or both of the carbonyl and sulfonyl oxygen atoms in its inorganic complexes [2–12], only a crystallographic study could unequivocally establish the nature of the intermolecular bridges in anhydrous triorganotin saccharin derivatives. Our attempt to prepare anhydrous triphenyltin saccharin gave, instead, the ethanol solvate, whose molecular structure is reported herein.

Experimental

Triphenyltin hydroxide and saccharin were dissolved in ethanol in a 1/1 molar ratio. Slow evaporation of the solvent gave large crystals of triphenyltin saccharin ethanol adduct, m.p. 242–244°C. Diffraction measurements were made on a Nicolet R3m/V four-circle diffractometer (graphite-monochromatized Mo-K_α radiation, λ 0.71073 Å), and determination of the crystal class, orientation matrix and accurate unit-cell parameters were performed according to established procedures [19]. Intensities were recorded at 20°C, and data collection and processing parameters are summarized in Table 1. The raw intensities were processed by the learned-profile procedure [20], and an absorption correction was based on a pseudo-ellipsoidal fit to azimuthal scans of 25 selected strong reflections over a range of 2θ

Table 1

Data collection and processing parameters

Molecular formula	$C_{25}H_{19}NO_3SSn \cdot C_2H_5OH$
Molecular weight	578.25
Unit cell constants	a 9.460(2), b 16.338(1), c 9.580(2) Å, β 113.76°, V 1355.2(4) Å^3; $Z = 2$
Density (calcd)	1.417 g cm^{-3}
Space group	$P2_1$
Radiation	graphite-monochromatized Mo-K_α, λ 0.71073 Å
Absorption coeff	10.38 cm^{-1}
Mean μr	0.204
Transmission factors	0.204
Scan type and speed	$\omega - 2\theta$; 2.02–8.37 deg min^{-1}
Scan range	0.65° below K_{α_1} to 0.65° above K_{α_2}
Background counting	stationary counts for one-half of scan time at each end of scan range
Collection range	h, k, $\pm l$; $2\theta_{max}$ 60°
Unique data measured	4114
Observed data with $\lvert F_o \rvert > 4\sigma(\lvert F_o \rvert)$, n	3917
Number of variables, p	307
$R_F = \Sigma[\lvert F_o \rvert - \lvert F_c \rvert]/\Sigma \lvert F_o \rvert$	0.050
Weighting scheme	$w = [\sigma^2 \lvert F_o \rvert + 0.008 \lvert F_o \rvert^2]^{-1}$
$R_G = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/\Sigma w \lvert F_o \rvert^2]^{1/2}$	0.074
$S = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/(n-p)]^{1/2}$	2.111
Residual extrema in final diff map	-0.50 to $+2.00$ eÅ^{-3}

values [21,22]. The structure was solved from the interpretation of a sharpened Patterson function. All non-hydrogen atoms in the asymmetric unit were subjected to anisotopic refinement. The benzene ring, methylene and methyl hydrogen atoms were generated geometrically and included in structural-factor calculations with their assigned isotropic temperature factors held constant. The hydroxyl hydrogen atom did not appear in the final difference map. All computations were performed on a DEC MicroVAX-II computer with the SHELX-PLUS systems [23]. Analytic expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were employed [24]. Blocked-cascade least-squares refinement [25], including an empirical isotopic extinction parameter $x = 4.8(8) \times 10^{-6}$ in the expression $F_{corr} = |F_c|/[1 + x|F_c|^2/\sin(2\theta)]^{1/4}$, converged to

Table 2

Atomic coordinates ($\times 10^5$ for Sn; $\times 10^4$ for other atoms) and thermal parameters [a] (Å$^2 \times 10^4$ for Sn and S; $\times 10^3$ for other atoms)

Atom	x	y	z	U_{eq}
Sn(1)	24208(4)	0	9603(4)	354(1)
S(1)	1892(2)	603(1)	4238(2)	402(6)
O(1)	1174(9)	1863(4)	817(7)	58(3)
O(2)	831(8)	−29(6)	4199(7)	61(2)
O(3)	3505(8)	469(5)	5272(8)	64(3)
O(4)	3127(8)	−783(4)	−772(7)	53(2)
N(1)	1789(8)	798(4)	2522(7)	40(2)
C(1)	1274(8)	1589(5)	4516(9)	42(2)
C(2)	1099(13)	1869(7)	5819(11)	62(4)
C(3)	574(15)	2694(7)	5700(15)	74(5)
C(4)	354(15)	3165(6)	4465(16)	73(5)
C(5)	574(11)	2859(5)	3236(12)	56(3)
C(6)	1034(8)	2053(4)	3277(9)	40(2)
C(7)	1327(9)	1596(4)	2087(8)	41(2)
C(8)	3015(9)	−1101(5)	2255(8)	41(2)
C(9)	4516(11)	−1253(6)	3297(9)	53(3)
C(10)	4942(14)	−2030(7)	3944(11)	66(4)
C(11)	3935(15)	−2633(6)	3593(12)	68(5)
C(12)	2515(18)	−2523(6)	2622(16)	80(6)
C(13)	2011(13)	−1772(6)	1908(12)	59(4)
C(14)	208(7)	63(6)	−839(7)	39(2)
C(15)	8(8)	67(7)	−2384(8)	45(2)
C(16)	−1457(10)	124(6)	−3562(9)	54(3)
C(17)	−2733(9)	135(6)	−3230(12)	63(3)
C(18)	−2616(9)	153(6)	−1761(12)	60(4)
C(19)	−1114(9)	107(7)	−531(10)	50(3)
C(20)	4296(8)	756(5)	1104(8)	41(2)
C(21)	4496(13)	1025(8)	−145(14)	59(4)
C(22)	5644(16)	1552(9)	−149(19)	85(6)
C(23)	6731(15)	1747(9)	1231(26)	108(9)
C(24)	6628(13)	1427(10)	2650(18)	95(6)
C(25)	5543(11)	997(7)	2553(12)	64(4)
C(26)	4381(14)	−1127(8)	−409(13)	62(4)
C(27)	4923(10)	−1408(5)	−1354(11)	50(3)

[a] Equivalent isotropic temperature factor U_{eq} defined as 1/3 of the trace of the orthogonalized U matrix.

Table 3

Selected bond lengths (Å) and bond angles (°)

Coordination around the tin atom			
Sn(1)-N(1)	2.240(7)	Sn(1)-C(8)	2.128(7)
Sn(1)-C(14)	2.111(5)	Sn(1)-C(20)	2.120(8)
Sn(1)-O(4)	2.394(8)		
N(1)-Sn(1)-C(8)	100.5(3)	N(1)-Sn(1)-C(14)	94.2(3)
N(1)-Sn(1)-C(20)	93.3(3)	N(1)-Sn(1)-O(4)	176.7(2)
C(8)-Sn(1)-C(14)	117.3(3)	C(8)-Sn(1)-C(20)	115.9(3)
C(8)-Sn(1)-O(4)	82.6(3)	C(14)-Sn(1)-C(20)	123.6(3)
C(14)-Sn(1)-O(4)	85.5(3)	C(20)-Sn(1)-O(4)	84.1(3)
Geometry of the saccharin group			
N(1)-C(7)	1.385(9)	N(1)-S(1)	1.639(8)
S(1)-O(2)	1.429(9)	S(1)-O(3)	1.463(6)
S(1)-C(1)	1.771(8)	C(1)-C(2)	1.400(15)
C(1)-C(6)	1.35(1)	C(2)-C(3)	1.43(2)
C(3)-C(4)	1.36(2)	C(4)-C(5)	1.37(2)
C(5)-C(6)	1.38(2)	C(6)-C(7)	1.48(1)
C(7)-O(1)	1.25(1)		
N(1)-S(1)-O(2)	110.9(4)	N(1)-S(1)-O(3)	109.4(4)
N(1)-S(1)-C(1)	94.8(4)	O(2)-S(1)-O(3)	116.1(4)
O(2)-S(1)-C(1)	113.0(5)	O(3)-S(1)-C(1)	110.5(4)
S(1)-C(1)-C(2)	126.6(7)	S(1)-C(1)-C(6)	109.1(7)
C(1)-C(2)-C(3)	114(1)	C(2)-C(3)-C(4)	122(1)
C(3)-C(4)-C(5)	121(1)	C(4)-C(5)-C(6)	119(1)
C(5)-C(6)-C(7)	127.9(8)	C(5)-C(6)-C(1)	120.0(9)
C(1)-C(6)-C(7)	122.2(7)	C(6)-C(7)-O(1)	126.3(7)
C(6)-C(7)-N(1)	112.2(7)		

the *R* indices listed in Table 1. Least-squares refinement with all atomic coordinates inverted (viz. reversal of the polar axis) yielded the same values for R_F and S as given in Table 1, so that the y coordinates of the lighter atom relative to Sn are not significantly affected by the choice of the absolute structure [26]. The final atomic coordinates are listed in Table 2. Bond distances and bond angles are given in Table 3. A complete table of structural parameters and lists of anisotropic thermal parameters and structure factors are available from the authors.

Discussion

The condensation reaction of triphenyltin hydroxide and saccharin in 95% ethanol yielded the ethanol adduct of triphenyltin saccharin. As depicted in Fig. 1, the molecule is five-coordinate at tin, and the geometry is *trans*-C_3SnNO trigonal bipyramidal. The ethanolic oxygen and the imido nitrogen atom of the saccharin ligand occupy the apical positions. The coordination polyhedron is distorted: the sum of carbon–tin–carbon angles in the equatorial plane (115.9(3), 117.3(3), 123.6(3)°; Sn–C 2.111(5), 2.120(8), 2.128(7) Å) is 356.8(9)° and the N(1)–Sn(1)–O(4) (Sn(1)–N(1) 2.240(7), Sn(1)–O(4) 2.394(8) Å) axial angle is 176.7(2)°. The tin atom is displaced out of the equatorial plane in the direction of N(1) by 0.221(1) Å. This plane and the benzisothiazole (C(1)–C(7), N(1), S(1)) plane are nearly perpendicular

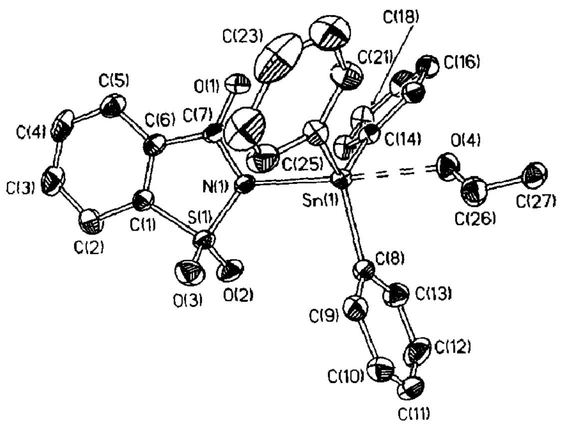

Fig. 1. Structure of triphenyltin saccharin ethanol adduct, drawn with atomic labeling.

to each other (dihedral angle 87(1)°). The three phenyl rings (C(8)–C(13), C(20)–C(25), C(14)–C(19)) make dihedral angles of 16(1), 42(1) and 120(1)°, respectively, with the equatorial plane. The carbonyl oxygen atom is 3.25(2) Å from the tin atom, but appears to be responsible for opening up the C(14)–Sn(1)–C(20) angle from the idealized 120° to 123.6(3)° (Sn(1)–N(1)–C(7)–O(1) torsional angle 4(1)°). The sulfonyl oxygen atoms are about 4 Å away from the tin atom, and if the molecule is viewed along the Sn(1)–N(1) vector, the C(8)–C(13) phenyl ring is seen to eclipse the sulfonyl group (C(8)–Sn(1)–N(1)–S(1) torsional angle is 4.2(7)°). The bond lengths and angles of the saccharin unit are not significantly different from the values reported for the free ligand [27].

There are few examples in the literature of organotin compounds containing both covalently-bonded nitrogen and coordinatively-bonded oxygen atoms. In addition to trimethyltin saccharin hydrate (Sn–N 2.30, Sn–O$_{water}$ 2.46 Å [13]), there are four examples of such systems involving carbonyl [28–31], two sulfonyl [17,18] and one nitro [32] donors. The Sn–N bond in trimethyltin succinimide [28] is 2.196 Å, but the long (2.600 Å) Sn ← O bond contributes to the distortion of the trigonal bipyramidal geometry; the structure of triethyltin succinimide [29] is similar. In the more distorted trimethyltin phthalimide [30], the Sn–N and Sn ← 0 bonds are 2.17 and 2.90 Å, respectively. The intermolecular carbonyl oxygen–tin distance in trimethylstannyl dimethylarsinyl(biscarbomethoxy)pyrazole [31] is even longer (3.32 Å) although the Sn–N bond is relatively short (2.18 Å), and the geometry is severely distorted towards the tetrahedral. In trimethylstannyl bis(trifluoromethanesulfonyl)methanesulfinamidine [17], the Sn–N bond is 2.345 Å; one of the sulfonyl oxygen atoms makes an intermolecular bond of 2.591 Å. In the trimethyltin derivative of 1,3,5-trithia-2,4,6-triazine-1,1-dioxide [18], the Sn–N and Sn ← O bonds are 2.218 and 2.822 Å. Trimethylstannylnitromethylamine, $(CH_3)_3SnN[N(=O) \rightarrow O](CH_3)$ [32], possess the dipolar nitro unit, so that the short Sn ← O distance of 2.36 Å is not unexpected.

Except for the stannylamine, the tin–oxygen bonds in the above compounds range from 2.46 to 3.32 Å. The relatively long intermolecular bonds reflect the generally reduced Lewis acidities of *N*-stannyl compounds. It may be inferred that in anhydrous triorganotin saccharins, any (carbonyl or sulfonyl) oxygen–tin interaction would be weak and readily disrupted in the presence of strongly coordinating donors, as appears to be the case in trimethyltin saccharin hydrate [13], which has the water molecule in the inner coordination sphere of the metal. The unexpected coordination of ethanol, rather than adventitious water, to triphenyltin saccharin is probably the consequence of steric inhibition of a hydrogen-bonded chain conformation (as that observed in the trimethyltin case), as much as of the general relief of steric strain in the molecule in going from the tetrahedral to the trigonal bipyramidal geometry. The title compound constitutes an unusual example of an organotin complex of an alcohol. In inorganic tin chemistry, a similar inner-sphere coordination has been demonstrated for $[Cl_3Sn(OC_2H_5) \cdot C_2H_5OH]_2$ (Sn–O 2.18 Å) [33].

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